

Crystal Growth In Aqueous Solutions

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Crystal Growth in Aqueous Solutions¹

I—Theory

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The following problem from the field of industrial crystallization is proposed: Given a saturated solution in which is suspended a known weight of seed crystals of known screen analysis, and assuming this solution to be cooled under known conditions, what will be the weight and screen analysis of the crystals at the end of the process if there is negligible formation of new nuclei?

A theoretical solution of this problem is developed. The fundamental postulates of this theory, which agree with other published researches are: (a) The actual yield should be very close to the theoretical yield. (b) The rate of growth of a face of a crystal, expressed as grams per square centimeter, is equal to the product of a specific constant pertaining to that face, and some function of the supersaturation of the solution. (c) The solubility differences due to particle size have a negligible effect on the growth of macroscopic crystals. (d) Each crystal, as it grows, remains substantially similar, geometrically, to its original shape.

It is shown that, if the above assumptions are true, geometrically similar crystals of the same material suspended in the same solution grow at the same rate if the growth is measured as the increase in length of geometrically corresponding distances on all of the crystals.

¹ Received July 3, 1928.

INDUSTRIAL crystallizations are often carried out, not only to obtain a maximum yield of pure solid material, as is the case in scientific work, but also to prepare crystalline particles of definite size distribution and crystal habit.

Before crystallization equipment can be rationally designed and intelligently operated, the laws that control the formation and growth of crystals must be known. Two steps are involved in the formation of macroscopic crystals from a saturated solution: first, minute crystalline aggregates, or nuclei, must form; and second, the nuclei must grow. This article is concerned with the second of these steps. The laws governing nucleus formation are not considered. The problem considered in this paper may be stated as follows:

Given a saturated solution in which is suspended a known weight of seed crystals of known screen analysis, and assuming this solution to be cooled under known conditions, what will be the weight and screen analysis of the crystals at the end of the process if there is negligible formation of new nuclei?

This problem is of importance because the more modern commercial crystallization processes are carried out by first forming nuclei and then allowing them to grow by slowly cooling the saturated solution in which they are suspended.

Previous Work

Although an enormous amount of theoretical and experimental work has been done on the symmetry, structure, habit, formation, growth, and solution of crystalline material, comparatively few researches have a direct bearing on this problem.

The work of Curie,² Lecoq de Boisbaudran,³ Berthoud,⁴ Wagner,⁵ Marc,⁶ Leblanc,⁷ Wenk,⁸ Valetton,⁹ Campbell,¹⁰ and Kukhareenko¹¹ on the geometry of crystals and the rate of crystal growth is important. In spite of some disagreement among these papers, certain conclusions can be drawn that have much evidence in their favor:

1—A crystal that grows under constant external conditions remains very nearly geometrically similar to its original shape.

2—The addition of small amounts of foreign substances may profoundly affect the shape of a growing crystal and its rate of growth.

² *Bull. soc. min.*, **8**, 145 (1885).

³ *Compt. rend.*, **80**, 1450 (1875).

⁴ *Bull. soc. Neuchatelois sci. nat.*, **33**, 122 (1904).

⁵ *Z. physik. Chem.*, **71**, 401 (1910); *Z. Elektrochem.*, **17**, 989 (1911).

⁶ *Z. physik. Chem.*, **61**, 385 (1907); **67**, 470, 640 (1909); **68**, 104 (1909); **73**, 685 (1910); *Z. Elektrochem.*, **16**, 201 (1910).

⁷ *Z. physik. Chem.*, **86**, 334 (1914); **77**, 614 (1911).

⁸ *Z. Kryst. Mineral.*, **47**, 124 (1909).

⁹ *Z. Krist.*, **59**, 135 (1923); *Ber. Verh. d. K. sächs. Ges. Wiss.*, **67**, 1 (1916); *Z. Krist.*, **59**, 335 (1923); **60**, 1 (1924).

¹⁰ *J. Chem. Soc.*, **107**, 475 (1915).

¹¹ *Centr. Zuckerind.*, **32**, 112 (1923); *Louisiana Planter*, **71**, 211, 231 (1923); *Sucr. Belge*, **46**, 131 (1926); **46**, 107 (1926); *Chimie & industrie*, Sp. No., 589 (May, 1927).

3—Different faces of the same crystal usually have different rates of growth.

4—Although the exact mechanism and the order of reaction of the growing process are not definitely known, it can be safely said that the rate of growth of any particular face in grams per square centimeter is a function of the supersaturation of the bulk of the solution in contact with that face.

5—It is very doubtful that the differences in solubility of the various faces of a single crystal, or of different size particles of the same material, are large enough to influence crystal growth unless the crystals are less than 0.002 cm. in diameter.

WORK OF MONTILLON—The only direct approach to the problem considered in this dissertation is the research carried out by Montillon,¹² who studied the growth of large numbers of seed crystals in a continuous glass crystallizer under carefully controlled conditions. A continuous apparatus was used because it could be more carefully controlled than could a batch apparatus. A large number of seed crystals were used to take advantage of the averaging effect of many nuclei.

Montillon's quantitative results were summed up in an empirical equation of the form:

$$10^{-3} \times \frac{\Delta W}{\Delta S} = ae^b \quad (1)$$

where ΔW is the increase in weight of the crystals during the process in grams per hour, ΔS is the increase in surface of the crystals in square centimeters per hour, θ is the time in minutes, and a and b are constants.

Data were obtained on Glauber's and Epsom salts at various temperatures. The value of a and b in equation (1) are given in Table I.

Table I—Values of Empirical Constants in Montillon's Equation

SALT	GLAUBER'S SALT			EPSOM SALT	
Temperature	27.1° C.	29.26° C.	30.90° C.	29.25° C.	31.6° C.
a	12.57	13.90	16.26	18.52	22.13
b	0.0178	0.0178	0.0178	0.0175	0.0175

Although equation (1) is frankly empirical, it fits Montillon's data very well. However, the main advance represented by this research was the development of a workable technic for investigating the process of crystal growth under conditions comparable to those used commercially.

Theoretical

The solution of the problem proposed depends on the answer of two questions:

1—How much material is precipitated?

2—How does the precipitating material distribute itself on the seed crystals?

The answer to the first question will determine the yield, and the answer to the second question will determine the size distribution and the screen analysis of the product.

¹² IND. ENG. CHEM., 19, 809 (1927).

Theoretical Yield

The first question is easily answered for most materials undergoing crystallization. Since crystallization is a slow process when nuclei do not form, and since there are a large number of crystals suspended in the cooling solution, no very great supersaturation can be expected at any stage in the process. It is true that the solution must be supersaturated to some extent or the crystals could not grow, but a very slight supersaturation will suffice. Indeed, if any considerable supersaturation should develop, a large number of new nuclei would form. This is contrary to the conditions of the problem. Therefore, it is to be expected that the solution will be very nearly saturated throughout the process and the difference in weight between the product and the seeds can be calculated from the amount of solution, the change of solubility with temperature, and the extent of cooling.

An exception to this statement occurs when the solution supports a high supersaturation without forming new nuclei, and has a high viscosity. The most important example of such slowly crystallizing substances is sucrose. For these cases the actual yield will be less than that demanded by the solubility curve, by the difference between the final and initial supersaturations.

Theoretical Screen Analysis

Consider a single crystal that is growing in a slowly cooled solution and kept in suspension by a suitable agitator. Let C denote the concentration of the bulk of the solution and C_0 the saturation concentration corresponding to the temperature of the crystal. Then the supersaturation is $C - C_0$. Each face of the crystal is, at any instant, growing at a definite rate that can be measured in grams per square centimeter per hour. The rate of growth of a face is proportional to some function of the supersaturation. The form of the function is unknown. It will be shown that the form does not have to be known. A differential equation can be written for each face. The equations for various faces are:

$$\begin{aligned}\frac{dW_1}{d\Theta} &= k_1 S_1 [f(C - C_0)] \\ \frac{dW_2}{d\Theta} &= k_2 S_2 [f(C - C_0)] \\ &\dots\dots\dots \\ \frac{dW_n}{d\Theta} &= k_n S_n [f(C - C_0)]\end{aligned}\tag{2}$$

where $W_1, W_2, \dots, W_n$ are the weights of material depositing on the different faces; $S_1, S_2, \dots, S_n$ are the areas of the faces; $k_1, k_2, \dots, k_n$ are the over-all reaction-rate constants of the faces; Θ is the time, and $(C - C_0)$ is the supersaturation of the solution surrounding the crystal. The total number of faces is n .

Since the crystal is growing under uniform external condi-

tions, it is at all times geometrically similar to its original shape.

If S is the total area of the crystal at the time Θ , then

$$\begin{aligned} S_1 &= a_1 S \\ S_2 &= a_2 S \\ &\dots\dots\dots \\ S_n &= a_n S \end{aligned} \quad (3)$$

where $a_1 + a_2 + \dots\dots a_n = 1$.

Because of the invariancy of the crystal shape, the fractions $a_1, a_2, \dots\dots a_n$ are constants during the growing process.

If the values of $S_1, S_2, \dots\dots S_n$ of equation (3) are substituted into equation (2) and the resulting equations added together, it is found that:

$$\frac{dW_1 + dW_2 + \dots\dots\dots dW_n}{d\Theta} = \frac{dW}{d\Theta} = (k_1 a_1 + k_2 a_2 + \dots\dots k_n a_n) (S) [f(C - C_0)] \quad (4)$$

where dW is the total increase in weight of the crystal.

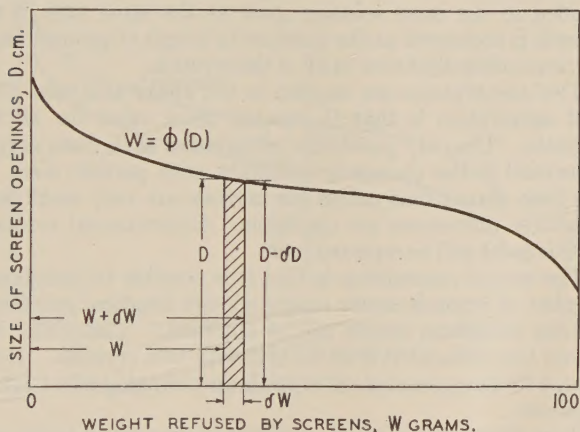


Figure 1—Cumulative Screen Analysis

If L is a linear distance between any two corners of a polyhedron, the weight and surface of that polyhedron are given by the expressions:

$$W = \rho b L^3 \quad (5)$$

$$S = c L^2 \quad (6)$$

where ρ is the density of the polyhedron and b and c are constants that are the equal for all geometrically similar solids provided L is the distance between corresponding points of the individual solids.

Since the crystal under consideration is growing under constant external conditions, equations (5) and (6) apply to all stages of the growth of the crystal and b and c are constants during the process.

From equation (5)

$$dW = 3 \rho b L^2 dL \quad (7)$$

(5)

Substituting values of S and dW from equations (6) and (7) into equation (4) the result is:

$$\frac{dL}{d\theta} = \frac{(k_1 a_1 + k_2 a_2 + \dots k_n a_n)(c)}{3 b \rho} [f(C - C_0)] \quad (8)$$

Since $k_1, k_2, \dots, k_n, a_1, a_2, \dots, a_n, \rho, b$, and c are all constants, equation (8) can be written as:

$$\frac{dL}{d\theta} = K[f(C - C_0)] \quad (9)$$

where K is a constant and is equal to $\frac{(k_1 a_1 + k_2 a_2, \dots k_n a_n)(c)}{3 b \rho}$

Consider, now, a second crystal of the same material, of the same geometric shape, and suspended in the same solution, but of different size than the first. If a differential equation is derived for this second crystal, it will be identical to equation (9) if the L 's of the two crystals connect geometrically corresponding corners. From this fact there follows an important principle:

All geometrically similar crystals of the same material suspended in the same solution grow at the same rate, if the growth is measured as the increase in length of geometrically corresponding distances on all of the crystals.

Two assumptions are implied in the above analysis. The first assumption is that C_0 has the same value for all the crystals. The only possibility of variation of C_0 from crystal to crystal is the change in solubility with particle size. It has been stated that unless the crystals are very small such solubility differences are negligible. Experimental evidence on this point will be reported later.

The second assumption is that it is possible to maintain a number of crystals under nearly enough identical conditions so that consistent results can be obtained. Campbell¹⁰ has shown how difficult it is to do this with two crystals. However, with large numbers of crystals an averaging effect can be expected.

Since every crystal grows at the same rate, the total growth of all the crystals will be the same. If ΔL is the increase in a linear dimension of one crystal, it is at the same time equal to the increase in the corresponding dimension of each of the other crystals, and is independent of the initial size of any of the original crystals.

This conclusion leads to a theoretical solution of the problem of predicting the screen analysis of the product if the screen analysis of the seeds and the yield are known.

The cumulative analysis of 100 grams of seeds can be plotted as shown in Figure 1. The significance of this plot is: The abscissa of any point on the curve represents the weight of crystals that will not pass through an opening of the size indicated by the ordinate of that point. If D is the size of the opening of a sieve and W is the weight of material that will not pass through this sieve, the plot of the cumulative screen analysis is the graph of the curve:

$$W = \phi(D) \quad (10)$$

There will be a definite size of crystal that will just pass through a given screen. This crystal will have a definite linear dimension, L . If all the crystals are geometrically similar, there will be a definite ratio between the value of L of any particular crystal and the size of the screen opening that will barely allow that crystal to pass. Assume that this ratio is the same for all the sieves. Mathematically, this assumption states:

$$\alpha D = L \quad (11)$$

where α is independent of D .

It will be desirable to obtain from the cumulative screen-analysis plot a cumulative plot of the number of crystals, N , against D . The abscissa of any point on this curve will represent the number of crystals that will not pass through a sieve of size opening equal to the ordinate of that point. As-

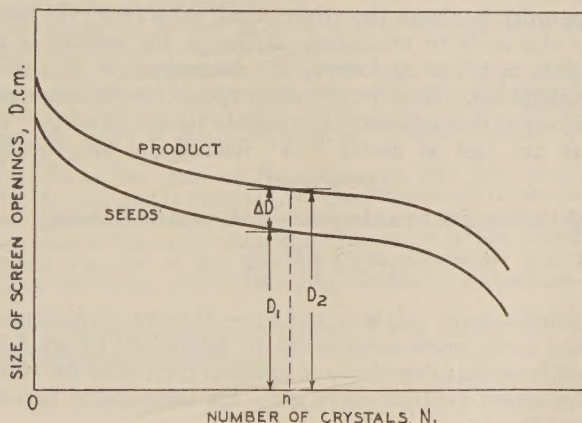


Figure 2— N vs. D Plot of Seeds and Product

sume that such curves have been drawn for the seeds and the product, and that the same axes have been used for both plots. These curves are presented in Figure 2. Consider seed crystal n . It will just pass through an opening D_1 cm. on a side. After growth it will just pass through an opening D_2 cm. on a side. Let ΔD represent this increase in D . Then, from equation (11)

$$\alpha \Delta D = \alpha(D_2 - D_1) = \Delta L \quad (12)$$

But α is a constant, and ΔL is identical for all the crystals. Therefore the vertical distance between the two curves of Figure 2 is constant for all points on the curves, and if one curve and the ΔD of one crystal are known the other curve can be constructed.

The construction of the N - D curves will now be described.

Consider, first, any point on the cumulative screen plot of the seeds. This point has the coördinates W and D . (Figure 1) These coördinates mean that, of the 100 grams

of seeds, W grams will not pass through a square opening measuring D cm. on a side.

Consider, next, a point very near to the point W, D . The coördinates of this second point are $W + dW$ and $D - dD$. Then, dW grams of seeds can be trapped between two screens having opening sizes of D and $D - dD$ cm. The average linear dimension of the crystals in the fraction dW is L , where $L = \alpha D$, the weight of a single crystal is ρbL^3 , and the number of crystals in the fraction is

$$dN = \frac{dW}{\rho bL^3} = \frac{dW}{\rho \alpha^3 b D^3} \quad (13)$$

The total number of crystals too large to pass through a screen opening D cm. on a side is:

$$N = \frac{1}{\rho \alpha^3 b} \int_0^W \frac{dW}{D^3} \quad (14)$$

In order to obtain the arithmetical value of N , the quantity $\alpha^3 \rho b$ must be evaluated. Although the density of the crystals, ρ , is usually known, the determination of α and b is bothersome. However, for the purpose of predicting screen analyses, it is unnecessary to evaluate these constants. The plots are just as useful if N' , defined by the equation

$$N' = \alpha^3 b N \quad (15)$$

is plotted against D , and equation (14) used in the form:

$$N' = \frac{1}{\rho} \int_0^W \frac{dW}{D^3} \quad (16)$$

Coördinates of points on the $N' - D$ curve corresponding to any given screen analysis can be determined by graphical or arithmetical integrations of equation (16), since the cumulative screen analysis curve gives the relationship between W and D .

Equation (16) can be written in the differential form for the seed crystals:

$$dN_s' = \frac{dW_s}{\rho D_s^3} \quad (17)$$

and for the product:

$$dN_p' = \frac{dW_p}{\rho (D_s + \Delta D)^3} \quad (18)$$

where the subscripts s and p refer to the seeds and product, respectively.

Since the same crystals form both seeds and product,

$$dN_s' = dN_p'$$

and, therefore,

$$\frac{dW_s}{D_s^3} = \frac{dW_p}{(D_s + \Delta D)^3} \quad (19)$$

it follows from equation (19) that

$$W_p = \int_0^{W_s} (1 + \Delta D/D_s)^3 dW_s \quad (20)$$

Since ΔD is independent of D_s and W_s , the value of W_p corresponding to any value of W_s can be obtained by graphical or arithmetical integration of equation (20), inasmuch as the screen-analysis curve of the seeds provides a relationship between D_s and W_s .

The steps in the calculation of the yield and screen analysis of the product on a crystal-growth process can now be outlined:

1—Calculate the theoretical yield from the ratio of seeds to solution and the solubility change of the material during the process.

2—Assume a value of ΔD and calculate the weight of the product that corresponds to this assumed value by integrating equation (20) over the range $W_s = 0$ to $W_s = 100$.

3—If the value of W_p calculated in step 2 does not check that calculated in step 1, adjust ΔD by trial and error until fair agreement is reached between the weights of product calculated by the two methods.

4—Using the correct value of ΔD , as determined in step 3, plot the integral curve of equation (20).

5—Plot W_p against D_p . This plot can be constructed from the data at hand at this point, since the integral curve plotted in step 4 gives the relationship between W_p and W_s , the screen-analysis curve of the seeds exhibits D_s as a function of W_s , and $D_p = D_s + \Delta D$.

6—From the curve of W_p against D_p that was plotted in step 5, read off the values of W_p that correspond to the sizes of the various screen openings, and convert the values to percentages of the entire product. The result is the cumulative screen analysis of the product. The differential analysis is easily derived from the cumulative analysis by subtraction.

The experimental confirmation of this theory will be described in a subsequent article.

II—Experimental

The theory of crystal growth presented in Part I is verified experimentally with potassium chloride and copper sulfate. Ten variables that might influence the process are investigated.

The experiments fall into two groups. The first group consists of a preliminary series of runs designed to test the assumption that the solubility differences due to particle size have but a negligible effect on the growth of macroscopic crystals. The second group consists of the main series of experiments that were designed to give a direct verification of the basic conclusion of the theory—namely, that the N' - D plots of the seeds and product of a crystallization process differ from each other only by a displacement along the D axis if the curves are plotted to the same pair of coordinate axes, where N' is proportional to the cumulative number of crystals caught on a screen of size opening D .

A THEORY of the growth of a large number of crystals in an aqueous solution, assuming that no new nuclei form during the process, has been advanced.¹ In this article the experimental verification of the theory is discussed.

EXPERIMENTS ON INFLUENCE OF CRYSTAL SIZE

In developing the theory it was assumed that the supersaturation of the solution in contact with growing crystals of macroscopic size is the same for all crystals, and independent of crystal size. Since the concentration of the bulk of the solution is maintained constant by agitation, this assumption requires that all the crystals, large and small, have the same solubility.

The experimental procedure consisted in suspending a mass of crystals of known weight and screen analysis in a saturated solution at constant temperature for a definite length of time, then filtering off the crystals and weighing and screening them. The two weights should be the same if the solution was saturated throughout the process and if the temperature control was accurate. If the small crystals were appreciably more soluble than the larger ones, a transfer of material from the smaller to the larger crystals would be expected, and the screen analysis of the crystal mass at the end of the process would show a larger percentage of coarse crystals and a smaller percentage of fine crystals than did the original batch. But if such solubility differences are negligible, the screen analyses of the crystals at the beginning and at the end of the process should be identical within the accuracy of the screen analyses. Four experiments of this type were carried out on potassium chloride crystals. The results are shown in Table I.

The changes in total weight of the crystals during the experiments were very small except in runs C and D, where there were 5 per cent increases, probably due to evaporation. It will be noted that, although the largest crystals were more than five times the size of the smallest ones, there is no systematic tendency of a growth of the larger crystals at the expense of the smaller, even when the crystals were in contact with a saturated solution for 18 hours.

EXPERIMENTAL DETERMINATION OF YIELDS AND N' - D PLOTS

Two predictions can be made from the theoretical analysis. First, for most substances the actual yield of a crystal-growth process should be practically equal to the theoretical yield; and second, the N' - D plots of the seeds and product should differ only by a constant difference measured parallel to the D axis. Most of the experimental work had as its object the direct verification of these two predictions of the theory. The yields and N' - D curves of actual crystal-growth processes were determined.

¹ IND. ENG. CHEM., 20, 30 (1928).

Description of Apparatus

The apparatus used by Montillon and Badger² after some modification was used for this work. The complete apparatus is shown diagrammatically in Figure 1.

The seed vessel (1) is equipped with a stirrer (2), a mercury-toluene thermostat (4), a thermometer reading to 0.05° C. (3), and a heating bulb (5) actuated by the thermostat (4). The purpose of this vessel is to mix the saturated solution from the mixing vessel (31) with seed crystals from feeder (39) and send the mixture at a constant temperature to the crystallizer tube (7).

The crystallizer tube (7) is a Pyrex glass tube 3 inches (7.6 cm.) in diameter and 5½ feet (1.67 meters) long, with a 1-inch (2.5-cm.) side tube (12) sealed in the side 4 inches (10.2 cm.) from the end. Tube (12) serves as a salt leg and crystal outlet. The purposes of the crystallizer tube are to provide a channel for the mixture of crystals and saturated solution from seed vessel (1) and to allow a slow, regular cooling of this mixture by the transfer of heat through the tube walls to the cooling water on the other side, and thus bring about a growth of the crystals. As the solution, free from crystals, leaves the crystallizer tube (7), its temperature is read by means of the thermometer (14) that reads to 0.05° C.

The pipe line (17) transports the impoverished solution from the crystallizer (7) to the suction of the glass pump (20). The solution is superheated in its passage to the pump by the electric resistance heater (18), which is controlled by the rheostat (19). This heater has two purposes: (1) by superheating the solution, freezing is prevented in the pump and pipe lines; and (2) the temperature of the liquid in the saturator (27) is controlled by this heater and its rheostat.

The pump (20) is constructed of Pyrex glass. The valves (22) are glass marbles that seat on rubber disks. The piston rod is made of brass, and the piston (21) consists of a rubber core wound with asbestos twine which is held in position by two copper disks and a lock nut. The brass parts are lacquered to prevent corrosion. An outlet (23) takes care of any leakage past the plunger (21). The pump discharge is controlled by varying the stroke of the piston and the r. p. m. of the pump.

The glass pipet (25) is for the purpose of measuring the rate of flow of solution. Cock (26) is closed and the solution is timed as it passes between two marks on the pipet cylinder. The volume between the marks is 100 cc.

Fitted into the saturator (27) is the top of a 3-liter beaker (29). A 60-mesh nickel screen is wired over the bottom of the beaker and a layer of salt about 3 inches (7.6 cm.) deep is piled on the screen. The saturator has two purposes: (1) the superheated solution from the pump is enriched as it percolates through the bed of salt; and (2) the salt bed acts as an effective filter and removes any suspended material that may be present in the solution. The saturator is fitted with a thermometer (28) reading to 0.1° C. and the temperature of this vessel is controlled by the rheostat (19).

From the saturator the solution passes through the siphon (30) to the mixing vessel (31), which is fitted with a stirrer (33), a thermometer (34) reading to 0.05° C., a 60-watt heating bulb (35), and a mercury-toluene thermostat (32). The purpose of this vessel is to provide a saturated solution at a definite temperature for the seed vessel (1). A mass of crystals is kept suspended in this vessel by the stirrer (33) and any residual under- or oversaturation remaining in the solution coming from the saturator (27) is rectified by the dissolving or growing of the crystals suspended in the mixing vessel. The outlet of the saturator is covered by a 60-mesh nickel screen (36).

² IND. ENG. CHEM., 19, 809 (1927).

Table I—Data Showing Lack of Influence of Crystal Size on the Growth of Crystals
(Temperature of all runs, 30° C.)

NOMINAL SCREEN	SCREEN OPENING	DIFFERENTIAL SCREEN ANALYSES							
		Run A		Run B		Run C		Run D	
		Original	After 2 hrs.	Original	After 2 hrs.	Original	After 10 hrs.	Original	After 18 hrs.
<i>Mesh</i>	<i>Cm.</i>	%	%	%	%	%	%	%	%
24	0.0701	0	0	0	0	1.82	1.27	1.35	0.82
28	0.0589	0.98	0.34	0.20	0.30	6.69	6.77	7.20	6.26
32	0.0495	11.71	10.00	8.40	8.25	9.69	9.59	3.82	3.48
35	0.0417	9.52	10.57	9.42	9.67	7.46	7.76	8.26	8.60
42	0.0351	18.94	18.59	16.85	15.95	8.36	7.93	8.29	8.01
48	0.0295	17.19	18.08	16.85	18.34	7.00	7.59	7.86	7.26
60	0.0246	8.73	8.49	9.14	9.63	7.00	7.77	8.27	8.10
65	0.0208	24.84	26.12	27.65	27.39	9.07	14.40	15.32	12.00
80	0.0175	Through 65	Through 65	0.34	0.67	0.37	0.48	0.51	0.50
100	0.0147	8.09	7.81	Through 80	Through 80	16.15	18.52	19.70	19.99
Through 100				11.15	9.80	31.07	24.26	19.42	26.98

The constant-level device (37) maintains a constant volume of solution in the mixing vessel (31). The by-pass (38) is used to drain the mixing vessel.

The cooling water reservoir (42) has a capacity of about 40 gallons (151 liters). It is equipped with a coil (43) which is connected to steam and cold-water lines, so the water in the reservoir can be rapidly heated or cooled to any desired temperature. When the temperature of the water has been brought to the correct point, it is maintained constant by the 100-watt incandescent bulbs (45) and the stirrer (44). The heat capacity of 40 gallons (151 liters) of water is so great that manual control of the heating bulbs (45) is accurate enough, and no thermostat is necessary. The temperature of the water in the reservoir is measured by a thermometer (46) which is graduated to 0.1° C.

The cooling-water circulating pump (47) is a small automobile water pump of the centrifugal type.

In order to remove suspended matter from the cooling water, two filters (49) are placed in the pipe line (48). The filters are connected in parallel and are constructed of standard pipe flanges and fittings. Each filter contains a brass screen supporting a thin layer of sand.

The cooling water, after filtering, passes into the angular space between the crystallizer (7) and its jacket (9). The rate of flow is controlled by the needle valve (50).

The crystallizer jacket (9) is a Pyrex tube 4 inches (10.2 cm.) in diameter and 5 feet (1.5 meters) long. The Bakelite disk (6) closes the crystallizer tube and jacket at the end near the seed vessel. The Bakelite disk (13) closes the crystallizer tube at the other end, while the brass ring (10) closes the annular space between the two tubes at the end where the crystals leave the crystallizer. Rubber gaskets, inserted in grooves, cushion the glass tubes where they engage the disks (6) and (13) and the ring (10). The ring and plates are held in place by the four brass tie rods (11, Figure 2) and suitable lock nuts. The jacket joints are smeared with vulcanized China wood oil to prevent leakage.

FEEDER—The mechanism of the feeder (39) is shown in detail in Figure 3. The essential parts are the three brass plates, *a*, *b*, *c*. The top plate, *a*, is connected to the funnel (40) by the pipe *f*. The bottom plate, *c*, is connected to the discharge pipe (41). The openings in the top and bottom plates are equidistant from the shaft, *d*, but are on different radii. The middle plate, *b*, is rotated by shaft *d* and contains one or more holes that are the same distance from the shaft as those in the stationary plates, *a* and *c*. As the shaft *d* is rotated by the worm gear *e*, an opening in the middle plate, *b*, passes under the opening in the top plate, *a*, a small volume of crystals falls into the opening of the middle plate, is transported between plates *a* and *c* until it is over the opening in the bottom plate, *c*, and falls through the feed pipe (41) into the seed vessel. The rate of feed is controlled by varying the r. p. m. of the worm *g* by means of a friction clutch on the shaft *h*.

CRYSTALLIZER—The assembly of the crystallizer tube, jacket, and Bakelite agitator is shown in Figure 2. The central shaft of the agitator, *m*, the spread rods, *n*, and the strips, *o*, are made of Bakelite. The rubber strips, *p*, sweep around the inside of the crystallizer tube, pick up the crystals, and shower them through the solution without crushing them. The brass bolts, *q*, tie the Bakelite and rubber strips together. The exposed parts of the bolts are lacquered.

As shown in Figure 1, the agitator shaft emerges from the crystallizer through a Bakelite stuffing box in the end plate (13) and is turned by the motor (15) working through the speed reducer (16).

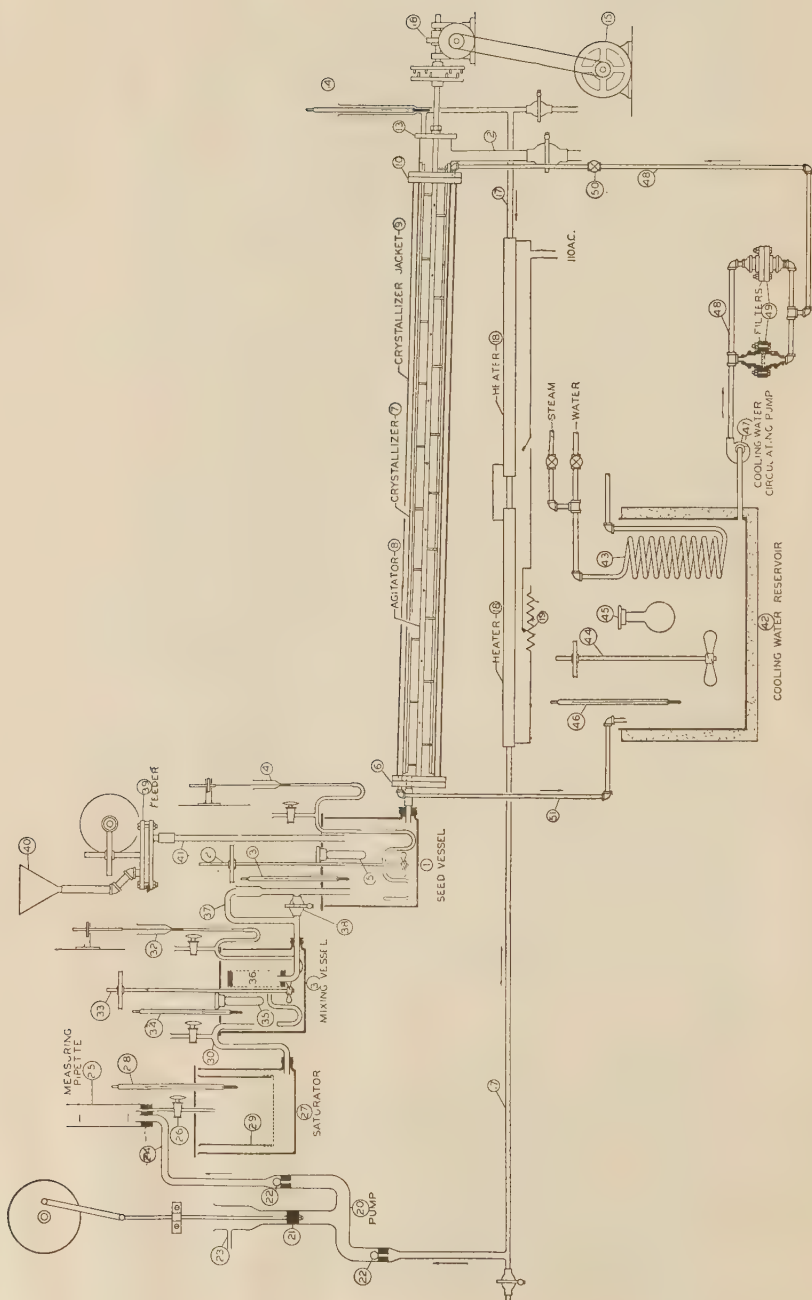


Figure 1—General Diagram of Apparatus

Properties of Materials

Two salts were used in this work. Most of the runs were carried out with potassium chloride, though several confirmatory experiments were run with copper sulfate pentahydrate. In all cases the solvent was water.

The solubilities and densities of the saturated solutions of potassium chloride were determined by the Earl of Berkeley.³

These data are fitted by the following empirical equations:

$$S = 28.22 + 0.3242t - 0.000498t^2 \quad (1)$$

$$\text{and } d = 1.1550 + 0.001076t \quad (2)$$

where S is the solubility of potassium chloride in parts per 100 parts of water, d is the density of saturated potassium chloride solution in grams per cubic centimeter, and t is the temperature in degrees Centigrade.

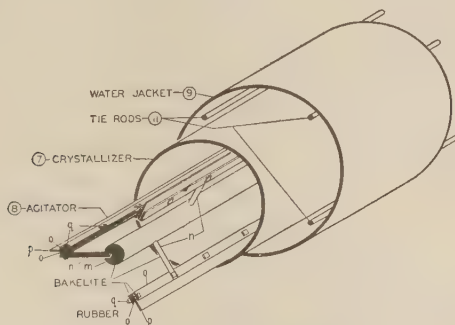


Figure 2—Detail of Crystallizer Tube

The density of potassium chloride crystals is 1.895.⁴

The solubility of copper sulfate is given by the empirical equation:

$$S = \frac{100(t + 46.48)}{198.4 - t} \quad (3)$$

where S is the solubility expressed in parts of copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) per 100 parts of "solvent" or "free" water, and t is the temperature in degrees Centigrade. The data that determine equation (3) are given in the standard handbooks.

There are no available data on the densities of saturated copper sulfate solutions.

The density of copper sulfate pentahydrate crystals is 2.27.⁵

Sources of Materials and Preparation of Seed Crystals

The potassium chloride used in this work was Mallinckrodt's "pure" grade. The material was pure enough to be

³ *Phil. Trans.*, **A203**, 207 (1904).

⁴ Baxter and Wallace, *J. Am. Chem. Soc.*, **38**, 70, 259 (1916).

⁵ Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. III, p. 240, Longmans, Green and Co., 1923.

used without recrystallization. It dissolved to a perfectly clear solution.

Two types of seed crystals were used in the potassium chloride experiments. The first type, used in most of the experiments, was prepared from the material as originally received by screening out the very coarse and very fine crystals. These seed crystals were mainly needles of somewhat irregular shape, although there were some cubical crystals present. The second type of seed crystal was prepared by recrystallizing the material in 3-liter batches under vigorous stirring. The material so obtained was in the form of roughly spherical crystalline aggregates, of marked difference in shape from the needle crystals.

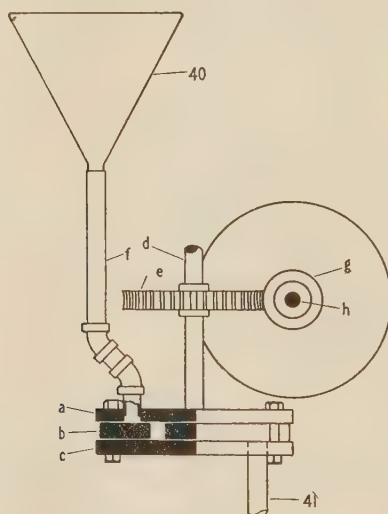


Figure 3—Detail of Feeder

The copper sulfate was recrystallized from commercial blue vitriol. The seed crystals were recrystallized in the same manner as were the spherical potassium chloride seeds. The copper sulfate seed crystals were very regular, with all axes developed to nearly the same extent.

Screen Analyses

All screen analyses of seeds and product were carried out with Tyler standard testing sieves. The intermediate screens were used in conjunction with the usual sieves.

It was found by trial that reasonably close checks of the screen analyses could be obtained if the samples were shaken in a Tyler Ro-Tap machine for half an hour, and if the size of any one fraction was less than about 20 grams. Usually samples of 25 to 50 grams were used.

Operation

For each run a sufficient amount of seed crystals was prepared, thoroughly mixed, and two samples taken. The solution was heated in an external jar with a steam coil to 10 or 15 degrees above the temperature of the run, and transferred to the apparatus. The water in the cooling water reservoir was also heated to several degrees above the final temperature, and cooling water and solution were circulated with the centrifugal and glass pumps. The saturator was nearly filled with crystals and excess crystals were added to the mixing vessel. The various temperatures were gradually brought to their proper points, and the taking of data started.

This preliminary part of the run required from 3 to 6 hours. No seed crystals were added during this time. When the temperatures and rates of flow had reached the desired values, the funnel of the feeder was filled with a known weight of seed crystals and the feeder started. Just before the feeder made its first dump, enough seed crystals were added to the seed vessel to bring the proportion of seeds to solution to the value desired for the run. The weight of crystals necessary to bring the seed to solution ratio to the correct value was calculated from the r. p. m. of the feeder, the rate of solution flow, the weight of crystals dumped per feeder revolution, and the volume of solution in the seed vessel.

When the entire apparatus was in smooth operation and the steady state reached, the following data were taken:

Every 10 minutes: the temperatures of the mixing vessel, seed crystal vessel, crystallizer exit, and cooling water reservoir, and, in later runs, the temperature of the saturator; the rates of flow of solution and cooling water.

Every 20 minutes: the weight of a feeder dump; the r. p. m. of the feeder.

At irregular intervals: the volume of leakage past the pump piston and the volume of solution accompanying the exit crystals. The solution from these sources was heated and poured back into the apparatus through the measuring pipet.

The crop that collected during the first hour or so after the start of the feeder was discarded to insure constant conditions through the crystallizer tube. For the next hour and a half the crop was saved. This is the time of the run proper. As fast as the exit tube filled with salt, it was drained into a Büchner funnel, filtered, and washed with alcohol. The crop for the run proper was saved, dried, and two samples were taken.

Screen analyses were made on each of the four samples (two of the seeds and two of the product) and average analyses of seeds and product calculated.

Typical Data Sheet

The data taken during a representative run, run 7, are shown in Table II. It will be noted that the temperature of the seed vessel was kept about 0.1 degree lower than that in

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Table II—Typical Data Sheet. Run 7

Time	TEMPERATURE			RATE OF FLOW		WEIGHT ONE FEEDER DUMP	SPEED FEEDER	SEED CRYSTALS	SOLUTION BY- PASSED	LEGS OF PRODUCT	REMARKS
	Mixing Vessel	Seed Vessel	Crystallizer Exit	Cooling Water	Solution						
P. M.	° C.	° C.	° C.	Sec./ 100 cc.	Cc./ 15 sec.	Grams	R. p. m.	Grams	Cc.		(2.26) (30) (32.5) = 39.0 56.5 First dump at 1:28
1:00	35.15	35.00	31.80	33.7	74	56.7	56.7				
1:10	35.10	35.05	31.80	30.8	74	56.4	56.4				
1:20	35.05	34.95	31.80	34.3	72	56.5	56.5	In seed vessel			
1:30	35.05	34.80	31.80	29.7	70	57.6	57.6	In feeder			
1:40	35.10	35.10	31.70	33.5	66			350.0			
1:50	35.10	35.00	31.80	29.0	114	2.27	58.0		300		
2:00	35.05	35.05	32.10	32.3	102	2.26	57.7		460		
2:10	35.05	35.10	32.20	30.9	102				70		
2:20	35.05	34.80	32.10	33.7	94	2.27	58.1		340		
2:30	35.05	34.85	31.95	33.7	94						
2:40	35.05	34.90	31.90	33.7	92				420	1	Start of run at 2:40
2:50	35.05	34.85	31.75	32.8	90	2.27	58.1		260	1	
3:00	35.00	35.00	31.75	33.5	86				450		
3:10	35.00	34.95	31.80	33.8	88	2.27	57.9		90		
3:20	35.05	34.80	31.85	29.5	86				390	1	Total crop = 349.8 grams
3:30	35.60	34.85	31.85	33.8	85	2.26	60.9			1	
3:40	35.00	34.90	31.90	31.8	82			In feeder	280	1	Total seeds = 376.7 grams
3:50	35.05	34.75	31.85	33.9	78			Left in feeder	250		
4:00	35.05	35.00	31.90	34.5	78						End of run 4:10
4:10	35.00	34.85	31.90			2.27	57.8		3310		
Av.	35.07	31.85		33.12							
Cor.	-0.17	-0.12									
	34.90		31.73								

the mixing vessel. This allows crystallization barely to start in the seed vessel.

The temperature and rate of flow of the cooling water, columns (5) and (7), were measured for purposes of control. The temperature of the solution leaving the crystallizer, column (4), was very sensitive to the temperature and rate of flow of cooling water.

The data in columns (8) and (9) were taken to give an independent check on the weight of seed crystals used. Any marked discrepancy between the actual weight and the calculated weight usually meant that the feeder clogged sometime during the run.

The first figure in column (10), 39.0 grams, was the weight of seed crystals added to the seed vessel to establish the correct proportion of seeds to solution. The two figures 350.0 and 44.7 are the weights of seed crystals put into the feeder funnel, while 18.7 grams of seeds were left over.

The volumes of solution that were collected from the pump leakage and the solution withdrawn with the product, column (11), are, in effect, a by-pass around the pump discharge.

The computation at the top of column (13) is the calculation of the initial mass of seed crystals added to the seed vessel. The volume of solution in the seed vessel is 3000 cc., or 30 dl. The weight of a feeder dump is 2.26 grams. The rate of solution flow is 32.5 seconds per deciliter, and the r. p. m. of the feeder plate is 56.5 seconds. There was one hole in the feeder plate—i. e., the feeder dumped once per revolution.

The screen analyses of the seeds and product of run 7 are given in Table III.

Table III—Differential Screen Analyses of Seeds and Product of Run 7
(Per cent retained on individual screens)

SCREEN	SIZE OF OPENING	SEEDS			PRODUCT		
		Sample I	Sample II	Av.	Sample I	Sample II	Av.
<i>Mesh</i>	<i>Cm.</i>	%	%	%	%	%	%
12	0.1397	0.00	0.00	0.00	0.00	0.00	0.00
14	0.1168	0.00	0.09	0.05	0.20	0.21	0.21
16	0.0991	1.78	2.03	1.90	4.16	4.57	4.36
20	0.0833	9.28	11.59	10.43	11.77	11.66	11.72
24	0.0701	11.01	12.16	11.58	11.75	12.15	11.95
28	0.0589	23.92	24.04	23.98	26.07	24.98	25.53
32	0.0495	19.41	18.33	18.87	20.00	19.25	19.62
35	0.0417	18.30	18.13	18.22	13.05	12.44	12.74
42	0.0351	12.64	10.91	11.77	2.14	2.10	2.12
48	0.0295	2.46	1.83	2.15	1.13	1.11	1.12
60	0.0246	0.31	0.26	0.29	1.49	1.52	1.50
Through							
60		0.89	0.63	0.76	8.24	10.01	9.13

Calculations on Typical Run

The theoretical increase in weight of the seed crystals during the process is calculated from the rate of flow of solution in grams per hour and the solubility change due to the cooling of the solution as it passes from the mixing vessel to the crystallizer outlet.

In run 7 the average corrected temperature of the solution in the mixing vessel is 34.90°C . (column 2, Table II). Substituting this value for t in equation (1), the concentration of the solution at this point is found to be 38.92 grams KCl per 100 grams H_2O . Also, using equation (1) and column (4), Table II, the concentration of the leaving solution is found to be 38.01 grams KCl per 100 grams H_2O . The total rate

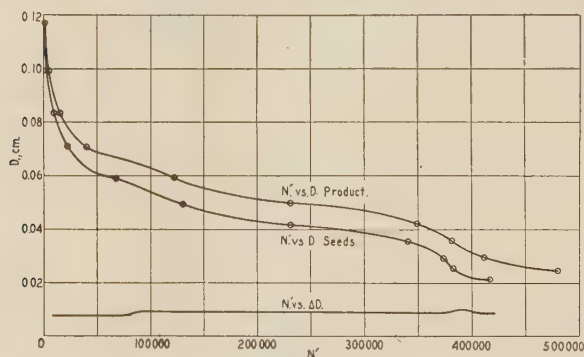


Figure 4—Run 7

of flow of solution, calculated from the average rate of flow through the measuring pipet (column 6) and the amount of solution by-passed (column 11), is 12,095 cc. per hour. The density of the solution is 1.189 as calculated by equation (2). The theoretical increase in weight is computed from these data and found to be 94.8 grams per hour, as compared with the figure found by actually weighing the seeds and product—

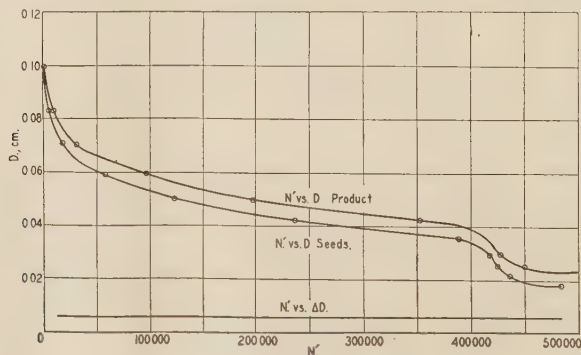


Figure 5—Run 10

namely, 93.7 grams per hour. The actual weight increase differs from the theoretical by 1.2 per cent. This difference is within the experimental error.

The weight of seeds used per hour, calculated from the data of columns 8 and 9 of Table II, is 141.5 grams per hour, which checks the figure obtained by weighing—namely, 139.5 grams per hour.

Table IV—

	POTASSIUM					
	4	5	6	7	11	12
1—Run	34.93	34.97	34.78	34.90	34.78	34.78
2—Mixing vessel temperature, ° C.	33.12	31.75	30.89	31.73	31.88	31.90
3—Crystallizer exit temperature, ° C.	8650	10,051	12,840	12,095	18,707	9895
4—Rate of solution flow, cc. per hour, total	123.3	117.2	127.3	139.5	267.1	134.9
5—Grams seeds per hour	167.3	196.5	253.1	233.2	399.9	201.6
6—Grams product per hour	44.0	79.3	125.8	93.7	132.8	66.7
7—Actual weight increase, grams	45.9	81.4	127.3	94.8	137.0	72.4
8—Theoretical weight increase, grams	-4.1	-2.7	-1.2	-1.2	-3.1	-7.9
9—Percentage error in actual weight increase						
10—Screen analysis of seeds:						
On 14 mesh	0.00	0.95	0.09	0.09	0.00	0.00
On 16 mesh	0.53	4.47	3.32	1.90	0.75	0.75
On 20 mesh	7.26	10.56	9.81	10.43	8.88	8.88
On 24 mesh	8.09	11.02	10.49	11.58	11.21	11.21
On 28 mesh	20.75	22.11	22.86	23.98	22.99	22.99
On 32 mesh	18.32	15.53	17.29	18.87	19.08	19.08
On 35 mesh	18.88	15.11	18.40	18.22	19.98	19.98
On 42 mesh	15.83	11.55	13.42	11.77	14.05	14.05
On 48 mesh	9.42	7.35	2.88	2.15	1.66	1.66
On 60 mesh	0.50	0.73	0.39	0.29	0.28	0.28
On 65 mesh	0.16	0.62 ^a	1.06 ^a	0.76 ^a	0.32	0.32
Through 65 mesh	0.22				0.81	0.81
11—Screen analysis of product:						
On 14 mesh	0.00	1.41	0.66	0.21	0.62	0.00
On 16 mesh	1.13	5.37	5.92	4.36	3.71	2.40
On 20 mesh	7.31	11.01	11.88	11.72	12.33	8.95
On 24 mesh	9.24	11.37	11.75	11.95	13.18	11.50
On 28 mesh	23.33	22.79	24.42	25.53	26.46	25.70
On 32 mesh	19.69	16.17	19.73	19.62	18.94	21.41
On 35 mesh	19.70	15.72	11.00	12.74	14.52	15.93
On 42 mesh	13.58	8.81	2.30	2.12	3.19	2.66
On 48 mesh	3.99	1.74	2.20	1.12	1.19	0.90
On 60 mesh	0.62	0.86	2.26	1.50	1.14	1.11
On 65 mesh	0.68	4.75 ^a	8.00 ^a	9.13 ^a	1.90	2.70
Through 65 mesh	0.73				2.81	6.60

^a Through 60 mesh.

Table V—Coordinates

SCREEN		D	KCl Needles						
			Run 4	5	6	7	11	12	14
Mesh									
Seed Crystals:									
14	0.1168	0	238	22	23	0	0	0	
16	0.0991	220	2,100	1,400	820	300	300	400	
20	0.0833	4,900	8,900	7,700	7,500	6,000	6,000	6,400	
24	0.0701	13,800	21,000	19,200	20,950	18,000	18,000	18,400	
28	0.0589	54,600	64,500	64,000	68,000	63,500	63,500	61,800	
32	0.0495	115,000	116,000	121,400	130,500	126,500	126,500	126,000	
35	0.0417	220,000	200,000	223,500	231,700	238,000	238,000	230,000	
42	0.0351	367,000	307,000	348,000	340,700	368,000	368,000	364,000	
48	0.0295	514,000	422,000	393,000	374,300	394,000	394,000	400,000	
60	0.0246	528,000	441,500	404,000	382,000	401,000	401,000	414,000	
65	0.0208	535,000	470,000 ^a	451,000 ^a	415,000 ^a	416,000	416,000	434,000	
Through 65	0.0175	552,000				477,000	477,000	505,000	
Products:									
14	0.1168	0	540	300	88	200	0	0	
16	0.0991	640	4,000	4,800	3,130	2,550	1,500	2,600	
20	0.0833	7,000	15,000	18,800	15,750	14,400	10,000	17,400	
24	0.0701	20,800	35,000	42,400	39,650	36,100	29,000	38,900	
28	0.0589	83,000	104,000	130,000	122,950	114,000	104,000	128,000	
32	0.0495	171,000	187,000	250,000	231,550	208,000	210,000	242,000	
35	0.0417	320,000	322,000	361,000	349,850	328,000	342,000	342,000	
42	0.0351	491,000	450,000	400,000	382,850	373,000	379,000	388,000	
48	0.0295	576,000	871,000	463,000	412,150	401,000	403,000	476,000	
60	0.0246	598,000	907,000	574,000	479,150	446,000	447,000	643,500	
65	0.0208	640,000	1,237,000 ^a	1,231,000 ^a	1,164,000 ^a	574,000	628,000	1,156,000	
Through 65	0.0175	714,000				889,000	1,367,000	2,504,000	

^a Through 60 mesh.

ental Data

NEEDLES						POTASSIUM CHLORIDE SPHERES			COPPER SULFATE		
18	19	23	25	8	10	22	27	28	29	30	31
38.88	39.06	30.95	39.82	35.03	34.75	31.87	34.98	33.72	34.96	40.16	33.60
36.34	36.31	28.94	37.30	32.01	31.90	30.12	32.37	31.25	33.44	37.96	32.11
9240	9370	19,780	9510	10,440	13,520	7725	9560	8400	8720	14,150	14,900
114.0	180.7	130.2	126.4	144.1	196.3	143.0	145.6	154.6	188.6	178.8	151.5
172.6	244.6	230.6	190.3	211.2	273.9	179.3	197.5	209.3	294.9	410.0	312.3
58.6	63.9	100.4	63.9	67.1	77.6	36.3	51.9	54.7	106.3	231.2	160.8
58.0	63.4	100.9	58.6	79.1	97.8	34.1	62.5	52.1	96.3	251.0	155.5
+1.0	+0.8	-0.5	+9.0	-15.2	-20.7	+6.5	-17.0	+5.0	+10.0	-7.9	+3.4
0.12	0.22	0.10	0.11	0.16	0.00			0.00	1.25	0.69	0.16
4.75	5.79	2.88	2.90	4.72	0.73		0.00	0.10	3.59	3.44	4.49
12.36	15.02	12.70	12.79	9.58	8.16	0.00	2.63	1.55	9.84	9.33	5.97
12.83	13.33	12.97	13.82	10.67	10.06	0.37	6.27	5.07	10.53	12.47	6.05
27.26	29.08	25.84	26.43	21.72	22.52	20.85	29.28	24.61	22.29	23.47	19.22
20.46	19.14	19.59	18.78	15.88	18.78	19.42	29.71	29.91	16.79	16.94	18.99
14.70	12.33	13.32	13.45	15.55	20.39	24.34	23.88	24.03	13.78	13.29	18.50
3.86	2.65	6.25	5.74	12.63	16.29	21.79	7.35	9.40	10.09	9.19	12.86
0.51	0.41	3.56	3.42	8.02	1.96	10.65	0.32	2.96	6.50	5.63	7.83
0.37	0.32	0.95	0.84	0.46	0.28	1.97	0.07	1.56	4.76	3.71	4.96
0.86	0.50	0.51	0.47	0.15	0.22	0.31	0.09	0.53	0.20	1.44	0.59
1.91	1.22	1.34	1.26	0.47	0.63	0.30	0.39	0.27	0.37	0.40	0.34
0.56	0.49	0.98	0.42	0.52	0.00		0.00	0.00	2.06	2.01	1.84
6.97	6.67	9.57	5.70	4.93	1.59		0.36	0.39	5.12	6.69	4.48
14.59	14.13	18.92	14.51	10.00	9.33	0.00	4.13	3.14	12.63	13.72	7.06
13.93	14.01	15.52	13.28	11.80	11.33	3.25	9.25	8.45	10.62	11.14	7.97
27.87	29.20	26.56	26.94	22.37	25.80	23.82	36.23	32.55	22.96	22.56	24.68
17.68	18.59	12.16	17.28	17.09	21.46	24.98	31.35	31.89	15.09	14.88	19.39
6.49	7.02	5.48	9.56	16.64	19.99	28.40	14.03	15.99	12.68	12.66	17.57
1.67	1.57	1.62	4.94	9.85	4.80	12.10	2.01	4.14	8.63	7.40	11.42
1.77	1.33	1.19	1.49	1.55	0.68	4.32	0.09	1.44	4.80	2.29	3.26
1.78	1.35	1.05	0.95	0.93	0.60	1.73	0.11	0.41	1.78	0.86	0.66
2.49	2.01	1.61	1.37	1.63	1.55	0.30	0.63	0.36	0.06	0.93	0.43
4.20	3.64	5.34	3.56	2.70	2.87	1.11	1.83	1.23	3.58	4.91	1.32

ts on *N'-D* Curves

VALUES OF *N'*

					Potassium Chloride Spheres			Copper Sulfate		
19	23	25	8	10	22	27	28	29	30	31
55	0	28	40	0			0	270	150	35
2,500	1,300	1,200	2,000	300		0	42	1,600	1,400	1,700
12,100	9,800	9,470	8,200	5,600	0	1,700	1,000	7,100	6,700	5,000
27,000	24,100	24,650	19,900	16,600	400	8,600	6,600	17,200	18,600	10,800
84,000	77,400	76,600	62,600	60,800	41,400	66,100	55,000	55,500	59,000	43,900
147,000	136,700	138,700	115,100	123,000	105,600	164,400	154,000	104,100	108,000	98,800
16,000	210,200	213,400	201,500	236,200	240,800	295,000	287,300	171,000	172,600	188,500
40,000	264,300	266,800	318,900	387,700	443,400	365,400	374,800	253,000	247,200	293,200
47,000	317,200	320,300	444,300	418,300	610,000	370,400	421,100	342,000	324,200	400,300
55,000	342,600	342,700	456,600	425,800	662,600	372,200	462,800	453,200	410,900	516,400
78,000	366,000	363,800	463,400	435,700	676,500	376,300	486,600	461,100	467,400	539,500
99,000	487,000	458,300	498,600	482,900	699,000	405,500	506,800	485,400	493,600	561,800
170	435	160	190	0			0	700	1,000	800
4,000	7,500	3,700	3,200	925		200	220	3,600	6,600	4,200
16,300	29,000	17,800	12,600	9,300	0	3,800	3,000	14,700	24,300	12,310
37,100	59,300	39,800	31,600	26,800	4,500	17,600	15,500	30,700	48,900	29,100
15,000	151,700	119,400	96,100	97,400	63,200	114,100	102,100	92,400	137,900	115,500
98,000	223,000	205,500	179,000	196,400	168,800	254,900	245,000	160,800	236,700	231,200
51,000	277,000	285,400	314,400	351,300	347,500	360,600	365,100	256,900	377,500	598,600
71,000	304,000	354,600	448,700	413,600	505,600	380,400	417,200	366,700	515,500	690,500
99,000	336,500	390,000	484,200	428,400	590,200	382,400	447,700	469,400	587,200	722,300
48,000	386,000	428,000	520,700	450,800	648,200	386,300	462,500	534,500	633,300	722,300
70,000	514,300	510,500	628,000	547,900	665,100	424,700	484,400	538,100	717,000	757,100
99,000	1,224,000	922,300	924,700	848,000	769,400	610,800	609,200	905,200	1,456,000	935,600

The N' - D curves of the seeds and product are obtained as shown in the theoretical development,² taking care that the total weight of the products is that equivalent to 100 grams of seeds. Figure 4 shows the N' - D plots of run 7. The vertical distance between the two curves is plotted as a ΔD vs. N' line. As required by the theory, this line is substantially straight.

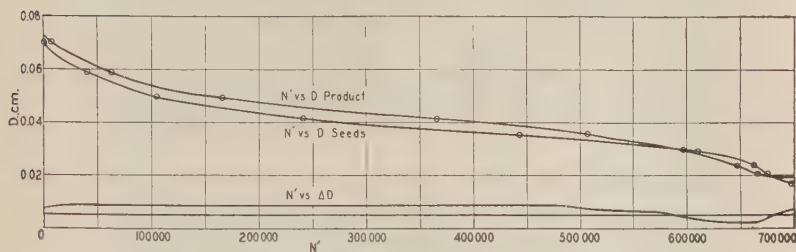


Figure 6—Run 22

Results

Thirty-one runs were made. Nineteen of these runs were satisfactory. The other twelve were either incomplete or obviously inaccurate and inconclusive. The nineteen runs included thirteen runs on potassium chloride needles, three on potassium chloride spheres, and three on copper sulfate pentahydrate. The results are given in Tables IV and V. The

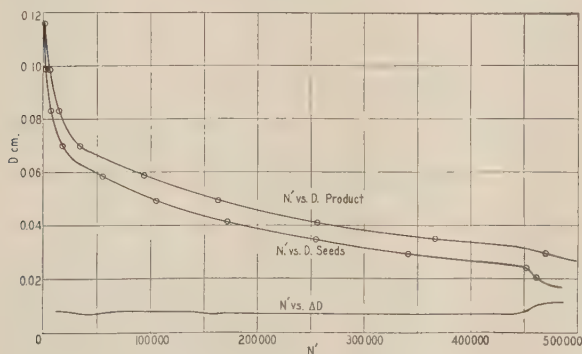


Figure 7—Run 29

N' vs. D Plots

coordinates of typical N' - D curves are plotted in Figures 4 to 7.

From the point of view of the theory developed above two criteria must be applied to each run. The first criterion is the agreement between the theoretical and actual yields; the second is the comparison of the N' - D curves of the seeds and product.

COMPARISON OF ACTUAL AND THEORETICAL YIELDS—The actual hourly increases in weight of the crystals as they passed

through the crystallizer are given in line (7) of Table IV. The theoretical hourly increases are given in line (8). Except for runs 8, 10, and 27, where the solutions in the seed vessel were known to be unsaturated, the theoretical and actual weight increases agree within 10 per cent in all of the runs (line 9). In ten of the runs the error is less than 5 per cent. The average algebraic error for all the potassium chloride runs, except runs 8, 10, and 27, is -0.07 per cent. The average algebraic error for the three copper sulfate runs is 2.0 per cent. It can be definitely stated, then, that the experiments check the assumption that nearly theoretical yields can be expected in crystal-growth processes of the kind considered in this article.

COMPARISON OF ACTUAL AND THEORETICAL $N'-D$ CURVES—
The relation between the $N'-D$ curves of the seeds and product of a run is even more important than that between the actual and theoretical yields. If the vertical distance between these curves at any point is ΔD , the theory demands that ΔD be

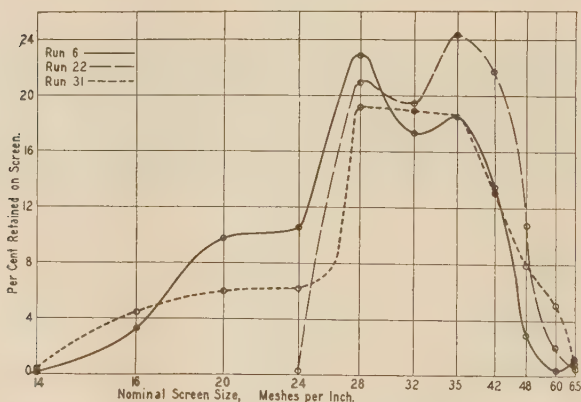


Figure 8—Typical Differential Screen Analyses of Seed Crystals

independent of N' . In other words, if values of ΔD are plotted as ordinates against values of N' as abscissas, a straight horizontal line should result. Accordingly, each of Figures 4 to 7 shows, in addition to the $N'-D$ curves of the seeds and product, an experimental $N'-\Delta D$ line. The correctness of the theory and the accuracy of the experiments are measured by the straightness of these lines. It will be recognized by glancing at Figures 4 to 7 that the $N'-\Delta D$ lines are substantially straight. It is true that some runs give straighter lines than others. It is also true that there are peaks and valleys. But there is no indication of any systematic divergence from the straight line demanded by the theory. The irregularities are more pronounced at the two ends of the lines than in the centers. This is to be expected. The ends corresponding to small values of N' also correspond to the greatest curvatures and changes in slope of the $N'-D$ lines, and the precision of the

N' - D lines suffers from these rapid changes in direction. The other ends of the curves correspond to the finer mesh screens, where slight errors in the screen analyses result in large relative errors in N' . For example, the value of $\delta N'$ for a gram of 14-mesh crystals of potassium chloride is 250, while that of a gram of 60-mesh material is 27,000. So it is not surprising that the ΔD - N' lines are less precise at the ends than in the middle. This statement will be checked later, when the observed screen analyses of the products of typical runs are compared with the theoretical analyses of these same runs. Figures 4 to 7 are representative of all the runs. The coördinates of the N' - D curves for the entire series are given in Table V.

VARIABLES OF GROWTH PROCESS—The validity of the relationships discussed above is best established by carrying out experiments in such a manner that the experimental conditions range over all the variables that might influence the crystal-growth process in aqueous solutions.

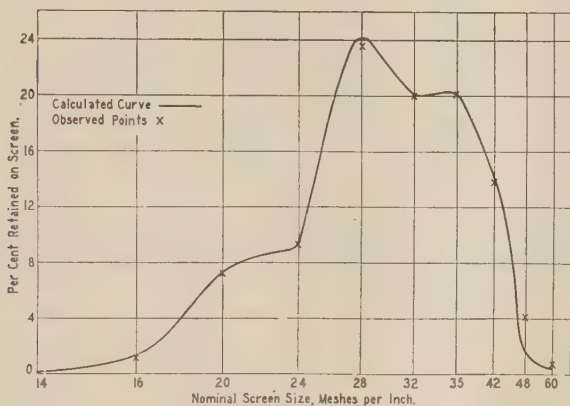


Figure 9—Product of Run 4

Analysis of the process leads to the following variables that should be so investigated:

- (1) Nature of solute
- (2) Crystallographic structure of crystals
- (3) Crystal habit of crystals
- (4) Temperature
- (5) Ratio of seed crystals to solution
- (6) Rate of precipitation of material
- (7) Weight ratio of product to seeds
- (8) Agitator speed
- (9) Screen analysis of seeds
- (10) Initial unsaturation of solution

The systematic investigation of the effects of these ten variables by varying one at a time and keeping nine constant would be not only tedious but unnecessary, since it is a question of checking a theory that takes into account all the variables, rather than developing an empirical relationship

among them. Accordingly, although all ten variables were investigated, the variations in them are not systematic. That this is so is apparent from Table VI, where the experimental conditions of the runs are summarized.

Table VI—Summary of Experimental Conditions for All Runs

RUN	AV. TEMPERA- TURE	WT. SEEDS PER 100 CC. SOLN.	ACTUAL WT. INCREASE	WT. PRODUCT PER GRAM SEEDS	AGITATOR SPEED
	° C.	Grams	Grams/hour	Grams	R. p. m.
KCl Needles					
4	34.0	1.22	45.9	1.36	18.2
5	33.4	1.17	79.3	1.68	18.2
6	32.8	1.18	125.8	1.99	18.2
7	33.3	1.15	93.7	1.67	18.2
8	33.5	1.38	67.1	1.47	18.2
10	33.3	1.45	77.6	1.40	18.2
11	33.3	1.43	132.8	1.50	18.2
12	33.3	1.37	66.7	1.49	18.2
14	37.1	0.84	112.6	1.93	18.2
18	37.6	1.23	58.6	1.51	18.2
19	37.7	1.93	63.9	1.35	18.2
23	29.9	0.66	100.4	1.77	11.4
25	38.6	1.33	63.9	1.51	11.4
KCl Spheres					
22	31.0	1.85	36.3	1.25	18.2
27	33.7	1.52	51.9	1.36	18.2
28	32.5	1.83	54.7	1.36	18.2
CuSO ₄ ·5H ₂ O Regular					
29	34.2	2.17	106.3	1.56	18.2
30	39.0	1.26	231.2	2.29	18.2
31	32.4	1.02	160.8	2.06	18.2

It will be seen from Table VI that the theory is checked experimentally for two solutes, potassium chloride and copper sulfate, which differ widely in chemical properties and crystal-

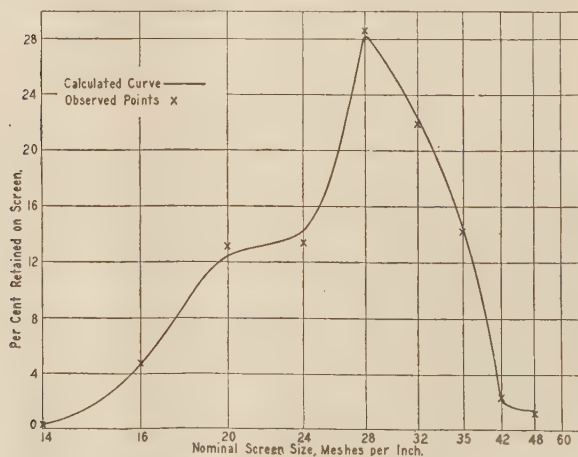


Figure 10—Product of Run 7

lographic structure; for three types of seed crystals—namely, spherical and needle agglomerates in the case of potassium chloride, and regular single crystals in the case of copper sul-

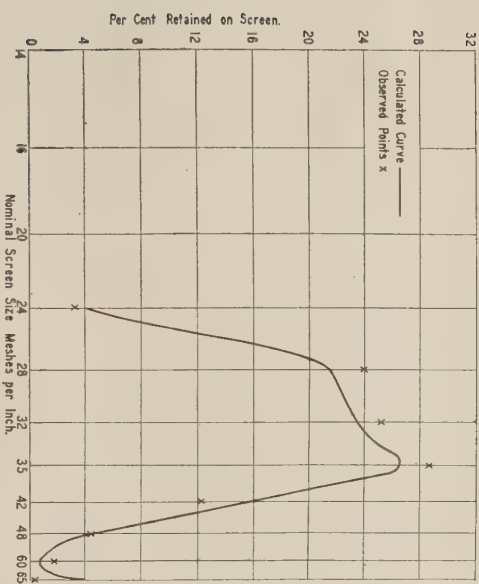


Figure 11—Product of Run 22

Comparison of Observed and Calculated Screen Analyses

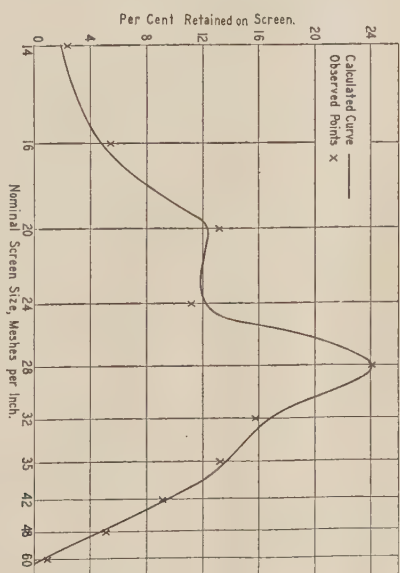


Figure 12—Product of Run 29

fate; over a temperature range of 29.9° to 39.0° C.; for ratios of seed crystals to solution from 0.66 to 2.17 grams per deciliter; for weight ratios of product to seeds from 1.25 to 2.29; and for two agitator speeds—11.4 and 18.2 r. p. m. Also, the screen analyses of the seeds varied widely, as shown in Figure 8. Furthermore, an initial undersaturation of the solution does not destroy the constancy of ΔD . (This is to be expected, since the dissolving process that precedes the crystallization process in such cases should be explained by the theory, provided the sign of the concentration difference is changed.) This fact is demonstrated by experiments 8, 10, and 27 (Figure 5).

In view of the experimental confirmations of the predicted effects of the ten variables discussed above, it is justifiable to state that the theory outlined in Part I applies very closely to crystal-growth processes.

FORMATION OF NEW NUCLEI—In the statement of the problem of this article it was postulated that the formation of new nuclei is to be negligible. The theory developed above conformed to this restraint. In the description of the experimental work and in the discussion of the results no mention has been made of nucleus formation. It is now necessary to consider the experiments from the point of view of the formation of new nuclei. The N' - D curves of the seeds and product of a run indicate whether or not new crystals were formed during that run. Since N' is proportional to the actual number of crystals, the two curves for the seeds and product will end at the same values of N' if no new nuclei are formed. If there are new nuclei, the N' - D curve for the product will extend beyond that of the seeds in proportion to the number of the new nuclei. It will be apparent from Table V that new nuclei were formed in all the runs to varying extents. It is necessary to determine what effect this extra phenomenon has on the use of the theory discussed so far. It will be recognized that the increase in weight of the solid during the process is made up of two parts: (1) that material which precipitates on the original seed crystals; (2) that which precipitates as new crystals. Furthermore, the screen analysis of the product is a combination of two analyses: (1) there is the analysis of the crystals grown from the original nuclei, and (2) there is the analysis of the new nuclei. Since the new nuclei must form before they can grow, and since the original nuclei have a start on the new ones, it can be reasonably assumed that substantially all of the original nuclei in the product will be larger than a certain definite size and that all of the new nuclei will be smaller than this same size. If this assumption is granted, the concepts of the corrected screen analysis and the corrected weight of the product become useful. The corrected screen analysis is the analysis of those crystals of the product that grew from the original seeds. It is obtained from the actual screen analysis of the product by taking from it the fine crystals formed as new nuclei. This

Table VII—Comparison between Observed and Calculated Product Screen Analysis (Cor.) for Typical Runs

SCREEN	KCl NEEDLES						KCl SPHERES						CaSO ₄	
	Run 4		Run 7		Run 18		Run 23		Run 22		Run 27		Run 29	
	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.
<i>Mesh</i>	%	%	%	%	%	%	%	%	%	%	%	%	%	%
14	1.15	1.15	0.23	0.24	0.70	0.59	0.95	1.05			0.39	0.37	1.84	2.16
16	7.41	7.41	4.69	4.85	8.23	7.37	9.28	10.28	4.04	3.29	4.47	4.22	4.57	5.36
20	9.11	9.34	12.96	13.12	13.74	13.44	13.98	20.33	21.50	24.07	9.34	9.46	12.26	13.23
24	9.11	9.85	14.12	13.97	13.74	14.74	21.05	16.68	23.26	28.73	37.34	37.02	24.07	11.12
28	23.06	22.88	28.13	28.86	30.80	29.45	25.52	28.55	26.42	26.26	32.38	32.04	16.69	24.05
32	20.23	19.86	22.31	21.96	18.84	18.70	14.35	13.07	15.93	12.23	14.39	14.33	13.64	15.80
36	20.94	19.86	14.32	14.26	6.50	6.87	7.39	5.89	4.36	4.37	0.82	2.05	9.32	9.04
42	14.79	13.77	2.10	2.37	0.78	1.87	2.68	1.74	1.75	0.12	0.12	0.09	4.88	5.03
48	1.77	4.04	1.42	1.25	0.82	1.88	1.86	1.13	0.30	0.36	0.36	0.11	0.83	0.94
60	0.38	0.63			1.15	1.32					0.39	0.31		
63														

can be done by cutting off the $N'-D$ curve of the product at the point where N' equals the terminal value of the $N'-D$ curve of the seed crystals. The corrected weight of the product is the weight of that part of the total product that results from the original seeds. It will be remembered that new nuclei were not considered when the $N'-D$ curves were computed. However, since the integration of the $N'-D$ equation is extended over the entire weight of the product, that part of the $N'-D$ curve that represents the corrected screen analysis is not affected by the new nuclei.

Since, in commercial operation, the fines from crystallization process are screened out, the final product is essentially the corrected product and has the corrected screen analysis.

COMPARISON OF OBSERVED AND CALCULATED SCREEN ANALYSIS—As a final check on the accuracy of the theory and experiments, the corrected screen analyses of the products of representative runs have been calculated from the screen analyses of the seed crystals of the same runs. The calculated analyses are compared with the experimental analyses in Table VII, and typical plots given in Figures 9 to 12. In these plots the full lines represent the calculated corrected screen analyses, and the individual points are the observed values. When it is remembered that errors of a screen analysis are ordinarily around 5 per cent, the checks are seen to be excellent except in the case of run 23, where the 20- and 24-mesh fractions are considerably in error. It very often happens that the division of particles between two large fractions in a screen test is poor. This is apparently what happened in run 23; screen 20 did not function properly, possibly on account of the meshes plugging up more than normally. Such difficulties are inherent in the screen method of determining size distribution.

It was pointed out above that the precision of the $N'-D$ curves at the ends corresponding to the small sizes is relatively poor. It will be seen from Table VII and Figures 9 to 12 that this low precision is of no practical consequence, because, since the calculations are reversed in passing back to the screen analysis of the product, the error irons out, and the calculated fractions of the small sizes check the actual fractions very well. For example, in run 22 the $N'-D$ curves of the seeds and product actually cross, owing mainly to the small value of ΔD for this run, and yet Figure 11 shows that the observed and calculated values of the fine sizes check within the accuracy of the ordinary screen analysis.

